II.F.11 University of Nevada Reno Photo-Electrochemical Project*

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*Congressionally directed project

Objectives

- Develop high efficiency metal oxide nanotubular array photo-anodes for generating hydrogen by water splitting.
- Develop density functional theory to understand the effect of morphology of the nanotubes on the photo-electrochemical properties of the photo-anodes.
- Develop kinetics and formation mechanism of the metal oxide nanotubes under different synthesis conditions.
- Develop combinatorial approach to prepare hybrid photo-anodes having multiple hetero-atoms incorporated in a single photo anode.
- Improve the durability of the material.
- Scale up the laboratory demonstration to production unit.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section (3.1.4.2.6) of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYRDDP):

(AP) Materials Efficiency
(AQ) Materials Durability
(AS) Device Configuration Designs

Technical Targets

This project is conducting research and development for potential application of TiO_2 nanotubes for hydrogen generation. Insights gained from these studies will be applied toward the design and synthesis of high efficiency materials for hydrogen generation from water splitting:

- Develop advanced renewable photo-electrochemical hydrogen generation technologies by 2015.

Approach

In this current project, utilization of hybrid titania nanotubular arrays for generation of hydrogen from water using sunlight is studied. The titania nanotubular arrays are robust, photo-corrosion resistant, and can be used in different electrolyte systems to generate hydrogen. It is envisioned that the process can be efficient and economical in the production of solar hydrogen. The nanotubular arrays are prepared by electrochemical anodization of solid titanium metal in different inorganic and organic electrolytes in the presence of fluoride ions. The effect of voltage, time, and solution chemistry on the size, uniformity, and self-assembly of nanotube formation is studied. Preliminary work has shown that an ultrasonic assisted process can generate a stable and efficient pattern of nanotubes that have excellent photo-efficiency. Materials prepared by organic solvents such as ethylene glycol and diethylene glycol also show enhanced activity for this purpose.

The hydrogen generation work is conducted using a hybrid titania nanotubes electrode in alkaline solutions in the presence of simulated solar light. The photo-efficiency is determined by measuring current as well as volume of hydrogen generated by gas chromatograph. The material stability and photo-efficiency is determined as a function of time.

In the future our main focus for the research will be to understand:

1. How TiO_2 nanotubes are different from TiO_2 nanoparticles with respect to charge transport characteristics.
2. Formation mechanism of TiO_2 nanotubes prepared by ultrasonic methods.

3. Formation mechanism and defect density in smooth and ridged nanotubes.
4. Effect of complex anions on the formation and kinetics of TiO_2 nanotubes.
5. Reaction kinetics of the water splitting reactions at the interface.
6. Effect of nanotubular wall thickness on electron trapping.
7. Electron trapping, e^-,h^+ recombination process in the nanotubes.
8. Effect of band bending across the nanotube wall.
9. Electron and hole mobility and their life time.
10. Stability of the nanotubes.

The methods will be adopted are as follows:

1. Laser flash spectroscopy.
2. Electron and hole titration.
3. Scanning Kelvin Probe Force microscopy
4. Hall probe.
5. Intensity modulated electrochemical impedance spectroscopy.

On the basis of fundamental and applied research, a scale-up experiment in the laboratory will be performed to elucidate the viability of titania nanotubes for photo-electrochemical generation of hydrogen using sunlight.

Accomplishments

- The UNR team has developed an innovative ultrasonically mediated fabrication process to synthesize hybrid titania nanotubes in a shorter time than conventional methods (50% reduction in time; Figure 1).
- UNR has also developed a method to prepare carbon doped hybrid titania nanotubes from ethylene glycol and diethylene glycol in a single step. These materials are also found to be highly efficient for generating hydrogen by water splitting (AM1.5 filter; applied potential 0.2 V with respect to a Ag/AgCl electrode; efficiency 6-8%; Figure 2). Samples prepared using ultrasonic treatment have better photoactivity than the conventional (magnetic stirring) method.

Special Recognitions & Awards/Patents Issued

1. Development of methods and devices for photo-electrochemical generation of hydrogen using hybrid titanium oxide nanotubes, U.S. Patent, filed Sept. 2005.

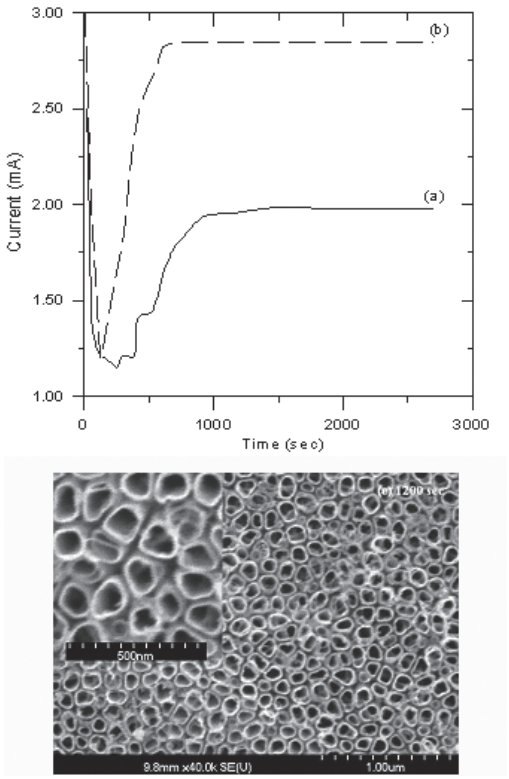

FIGURE 1. (top) Current vs time graph during anodization of Ti in 0.5M H_3PO_4 and 0.14M NaF solution using (a) magnetic stirring and b) ultrasonic. (bottom) SEM image of TiO_2 nanotubes prepared using ultrasonic treatments and aqueous phosphoric acid.

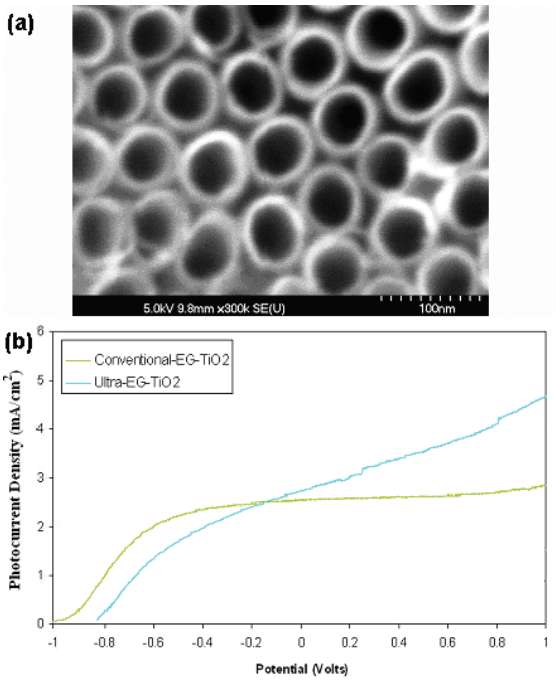

FIGURE 2. (a) SEM image of the TiO_2 nanotubular arrays prepared by ultrasonic treatment and ethylene glycol. (b) Photo-current density of the titania photo-anodes prepared by ultrasonic treatment and ethylene glycol.

FY 2006 Publications/Presentations

1. "Determination of Photo Conversion Efficiency of Nanotubular Titanium Oxide Photo-electrochemical Cell for Solar Hydrogen Generation" J. Power Sources, 2006, in press, doi:10.1016/j.jpowsour.2005.12.036.

2. "Photo-electrochemical Hydrogen Generation using Band-gap Modified Nanotubular Titanium Oxide in Solar Light" J. Power Sources, 2006, in press, doi:10.1016/j.jpowsour.2006.06.044.

3. "Photo-electrochemical Generation of Hydrogen Using Hybrid Titanium Dioxide Nanotubular Arrays" to be presented in SPIE August 13-17, 2006.